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<p>(21) International Application Number: PCT/AU83/00098 (22) International Filing Date: 2 August 1983 (02.08.83) (31) Priority Application Numbers: PF 5226 PF 7224 (32) Priority Dates: 5 August 1982 (05.08.82) 10 December 1982 (10.12.82) (33) Priority Country: AU (71) Applicant (for all designated States except US): DEX- TEC METALLURGICAL PTY. LTD. [AU/AU]; 124 Walker Street, North Sydney, NSW 2060 (AU). (72) Inventor; and (75) Inventor/Applicant (for US only) : EVERETT, Peter, Kenneth [AU/AU]; 63 Victoria Avenue, Chatswood, NSW 2067 (AU). (74) Agent: COWIE, THOMSON & CARTER; 71 Queens Road, Melbourne, VIC 3004 (AU).</p>		<p>(81) Designated States: AU, BR, DE (European patent), FI, FR (European patent), GB (European patent), JP, NO, SE (European patent), US. Published With international search report.</p>
<p>(54) Title: RECOVERY OF SILVER AND GOLD FROM ORES AND CONCENTRATES</p> <p>(57) Abstract</p> <p>Process for the dissolution of silver and gold from ores and concentrates in a strong chloride solution where the Eh is maintained above a value of 750 m.v. and preferably above a value of 850 m.v. This process may include the additional step of removing excess chlorine from solution by blowing the solution with air and conducting the air and chlorine gas to another vessel where the chlorine is reacted with fresh incoming ore or concentrate. Subsequently the substantially chlorine free solution is contacted with a solid reductant to produce silver or gold precipitate. The above process is particularly suitable for operation in an electrochemical diaphragm cell.</p>		

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RECOVERY OF SILVER AND GOLD FROM
ORES AND CONCENTRATES

FIELD OF THE INVENTION

Background of the Invention

5 This invention relates to a hydrometallurgical method of recovering silver and/or gold from ores and concentrates. Particularly it applies to ores which are not easily treated by normal methods.

10 Many silver and gold bearing ores and concentrates are treated by flotation and cyanidation. This can often lead to low recoveries due to the variety of mineralization which may be present. For example it is known that many ores containing appreciable quantities of manganese are treated with low recoveries.

15 Description of the Prior art

 In Australian Patent Application 75848/81, "Recovery of Silver and Gold from Ores and Concentrates", there is described a process for the treatment of minerals that are not easily treated by traditional flotation and cyanidation processes. In this respect, it has been found possible to leach many Ag bearing materials by using a strong chloride solution. Typically strong chloride solution may be used:

- 25 a) without oxidation;
 b) with air oxidation;
 c) with air oxidation using a Cu catalyst; and
 d) oxidation using chlorine.

30 Further investigations have revealed that for some silver and/or gold ores or concentrates, the use of a strong oxidant is still not effective enough under normal process conditions.

The Invention

The present invention relates to the treatment of minerals, where not only must a strong oxidant such as chlorine be used, but a high oxidation potential must be maintained in the solution to prevent reprecipitation of the Ag.

Preferred Aspects of the Invention

Accordingly, there is provided in one aspect of the invention, a process for the recovery of silver and/or gold from a silver and/or gold bearing ore or concentrate which includes

- 1) forming a mixture of ore or concentrate and a strong electrolyte containing chloride ions,
- 2) maintaining the mixture at a temperature up to the boiling point of the electrolyte whereby the silver and/or gold is taken into solution,
- 3) maintaining an oxidation potential of the solution above about 750 m.v. with reference to a hydrogen electrode, and
- 4) recovering silver and/or gold from the solution.

In another aspect of the invention, there is provided a process for the recovery of silver and/or gold from a silver and/or gold bearing ore or concentrate which includes

- 1) forming a mixture of ore or concentrate and a strong electrolyte containing chloride ions, in an anolyte compartment of a cylindrical diaphragm cell, the cell also including an anode, a cathode and a catholyte compartment,
- 2) maintaining the mixture at a temperature up to the boiling point of the electrolyte whereby the silver and/or gold is taken into solution,
- 3) passing current between the anode and cathode to maintain an oxidation potential of the solution above about 750 m.v. with reference to a hydrogen electrode,
- 4) recovering silver and/or gold from the solution.



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Preferably the oxidation potential (Eh) is maintained above about 850 m.v. It has been found by keeping the Eh above about 750 m.v. that reprecipitation of silver and/or gold is inhibited.

- 5 To effect control of the Eh, it is convenient to add a source of chlorine. This source of chlorine is usually chlorine gas or hypochlorite ion (e.g. sodium hypochlorite). Alternatively, it is possible to effect the control of Eh by passing a current through the mixture.
- 10 Typically only intermittent passage of current will be necessary. As such it is possible to significantly reduce the chlorine requirement of the process.

- Preferably prior to introducing a source of chlorine, an oxygen bearing gas is introduced into the mixture. This reduces the amount of chlorine subsequently required. When chlorination does occur, it is preferably carried out at a pH of approximately 7.
- 15

- Where substantial amounts of chlorine are introduced, the resultant solution contains free chlorine. This free chlorine is recovered from the solution by blowing oxygen bearing gases through the solution prior to recovery of the silver and/or gold. To enhance the efficiency of process, the mixture of free chlorine and gas is conducted to another vessel containing fresh ore or concentrate, to effect a preliminary oxidation.
- 20
- 25

- Desirably the recovery of silver and/or gold is achieved by precipitation via contact of the solution with a reductant. The reductant may be a metal (iron or steel) having a potential above that of silver and/or gold in the electrochemical series.
- 30

- When iron or steel is employed, it is usual to form a column of elongated iron or steel members e.g. rods. Typically the solution is passed through the column and by contacting the surface of the members the silver and/or gold is precipitated. To ensure recovery of the precipitated silver and/or gold from the steel or iron members, it is desirable to either vibrate the column or
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increase the volume of solution flowing therethrough. Thus the silver or gold powder will collect in the bottom of the column and be easily removed.

- With regard to the pH of the solution during treatment of the ore or concentrate, it will be well known to those skilled in the art that same is normally set according to the type of ore or concentrate. For example it is preferable to treat carbonate containing ores or concentrates at a pH of about 7. At this level the material is stable. Similarly if the ore or concentrate contains sulphides, it is preferable to carry out the reaction at a pH of below 7. Typically when one is recovering gold a preferred pH is above 5 and more preferably about 7. Thus it is to be understood that the present invention is not restricted to a pH of a particular range.

Examples

- An Ag bearing mineral was slurried with a strong chloride solution, 25% NaCl, and aerated for 1 to 2 hours at approximately 20°C to treat any easily oxidizable material present. This preliminary aeration can reduce the amount of chlorine required for the Ag leaching in the next step. After the aeration, chlorine was added to the slurry mixture in the form of sodium hypochlorite or preferably chlorine gas, and the oxidation potential (Eh) maintained above a value of 750 m.v. The chlorination was preferably carried out at a pH of approximately 7.0. Table I shows the leaching and reprecipitation of the Ag from solution when the Eh was allowed to fall below 750 m.v. Table II shows the leaching and high recovery of Ag from this particular mineral when the Eh was maintained above 850 m.v. throughout the test.



Leaching of Silver Ores

Slurry Density 300 g/l - NaCl 250 g/l - Temperature 30°C

Table ITable II

	Eh(mv)	Ag (ppm) in soln.	Eh(mv)	Ag (ppm) in soln.
5	780	25	850	55
	765	26	855	59
	725	23	866	66
10	740	16	893	69
	726	11	892	73
	440	3	865	74
	Feed 260 ppm Residue 250 ppm		Feed 260 ppm Residue 9 ppm	

- 15 The solution was separated from the solids by filtration or counter-current decantation and because of the Eh requirement of greater than about 850 m.v. the solution contained free chlorine. The solution pH was adjusted to approximately 2.5 to 3.0 and air was blown
- 20 into the solution to remove free chlorine with the exit gases. These gases were conducted to another vessel containing a new batch of ore, to effect a preliminary oxidation. When the chlorine removal step had been accomplished the new batch of ore then proceeded to the
- 25 chlorination stage where the Eh was maintained above 850 m.v. The chlorine free solution was passed to a vessel where it was contacted with a metallic iron reductant. Typically, this operation was effected by passage of the electrolyte down a column of vertical steel
- 30 rods, for example 2 mm diameter. The Ag formed a powdery deposit on the surface of the iron. Periodically the column was either vibrated slightly or the solution flow adjusted to accomplish the removal of Ag from the iron surface resulting in collection of the powder in the



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bottom of the column.

It was found in many examples that large amounts of chlorine were required, rendering the process potentially uneconomic. The following example was one where the cost of chlorine was high.

Six kilos of ore assaying 160 ppm of silver were agitated in 20 litres of 25% NaCl in a 25 litre tank. Chlorine was admitted from a cylinder through a measuring apparatus to the sealed tank periodically to maintain the oxidation potential above 850 m.v. Over a 5 hour period the silver was liberated with a final Ag concentration in solution of 40 ppm Ag. The analysis of the residue showed 20 ppm Ag. The chlorine usage however was 35g for the 6 kilos. The cost of the chlorine was a large part of the value of the recovered silver.

The following examples illustrate the leaching of gold under these conditions.

Chlorine was added to slurries of ore (300 g/l) in sodium chloride solution (300 g/l NaCl) to maintain the Eh above 750 m.v. The pH was varied between pH 3.0 and 8.0.

	<u>Sample</u>	<u>Au Content (ppm)</u>
	Feed	7.8
	Residue from pH3 test	6.2
	Residue from pH4 test	5.5
25	Residue from pH5 test	0.8
	Residue from pH6.5 test	0.5
	Residue from pH8 test	0.3

These results showed the improved leaching of gold under these Eh conditions at a pH of over 5.0.

The following example shows how electrochemical techniques can be used to overcome these high costs.

A cylindrical diaphragm cell was provided to achieve maximum anolyte volume for treatment of low grade ores with a small catholyte volume on the outside of the cylindrical diaphragm, in a cylindrical tank. Current was passed



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between the anodes, for example graphite, and a high surface area cathode, for example copper, while the silver and/or gold bearing ore was agitated slowly in the anolyte compartment. Hydrogen may have been liberated at the cathode to form sodium hydroxide, and oxidized chlorine species may have been formed at the anode. Some mixing of the anolyte and the catholyte may have resulted in the formation of such compounds as NaOCl.

The following example illustrates the operation of an embodiment of this process, carried out, in a cylindrical diaphragm cell of the type illustrated and labelled in the accompanying drawing.

6 kilos of ore assaying 160 ppm of silver were agitated in 20 litres of 25% NaCl in a 25 litre cylindrical diaphragm cell. The current was turned on periodically to maintain the oxidation potential above 850 m.v. with reference to the saturated hydrogen electrode. Over a 4 hour period, current was passed at 2 amps, and 3.4 volts, for a total of 30 minutes. The theoretical amount of chlorine generated by this method would be 1.55 grams. The solution analysed 41 ppm Ag and the analysis of the solid residue showed a concentration of 16 ppm Ag. This resulted in a theoretical chlorine usage of 1.79 grams/gram Ag.

Although the example of the embodiment is described according to the liberation of chlorine at the anode, it will be appreciated that many different compounds can be generated.

The method and apparatus of the invention results in a greater than 20 times reduction in reagent costs. Obviously, this is a significant improvement over previous proposals involved with the use of chlorine gas.



Claims

1. A process for the recovery of silver and/or gold from a silver and/or gold bearing ore or concentrate which includes
 - 1) forming a mixture of ore or concentrate and a strong electrolyte containing chloride ions,
 - 2) maintaining the mixture at a temperature up to the boiling point of the electrolyte whereby the silver and/or gold is taken into solution,
 - 3) maintaining an oxidation potential of the solution above about 750 m.v. with reference to a hydrogen electrode, and
 - 4) recovering silver and/or gold from the solution.
2. A process according to Claim 1 wherein the oxidation potential of the solution is maintained above about 850 m.v.
3. A process according to either Claims 1 or 2 wherein an oxygen bearing gas is introduced into the mixture.
4. A process according to any one of Claims 1 to 3 wherein a source of chlorine is added to the mixture.
5. A process according to Claim 4 wherein the source of chlorine is chlorine gas or hypochlorite ion.
6. A process according to Claim 4 wherein the pH of the mixture is approximately 7.0.
7. A process according to Claim 1 wherein an oxygen bearing gas is blown through the solution prior to the recovery step (4), to form a mixture of said gas and free chlorine.
8. A process according to Claim 7 wherein the mixture of said gas and free chlorine is admixed with fresh silver and/or gold bearing ore or concentrate.



9. A process according to any one of Claims 1 to 8 wherein the recovery includes contacting the solution with a reductant to precipitate silver and/or gold.
10. A process according to Claim 9 wherein the reductant is a metal having a potential above that of silver and/or gold in the electrochemical series.
11. A process according to Claim 9 wherein the reductant is iron or steel.
12. A process according to Claim 9 wherein the precipitation is carried out in a column containing a plurality of elongated iron and steel members.
13. A process according to Claim 12 wherein the column is vibrated.
14. A process according to Claim 12 wherein the solution is turbulent within the column.
15. A process for the recovery of silver and/or gold from a silver and/or gold bearing ore or concentrate which includes
- 1) forming a mixture of ore or concentrate and a strong electrolyte containing chloride ions, in an anolyte compartment of a cylindrical diaphragm cell, the cell also including an anode, a cathode and a catholyte compartment,
 - 2) maintaining the mixture at a temperature up to the boiling point of the electrolyte whereby the silver and/or gold is taken into solution,
 - 3) passing current between the anode and cathode to maintain an oxidation potential of the solution above about 750 m.v. with reference to a hydrogen electrode,
 - 4) recovering silver and/or gold from the solution.

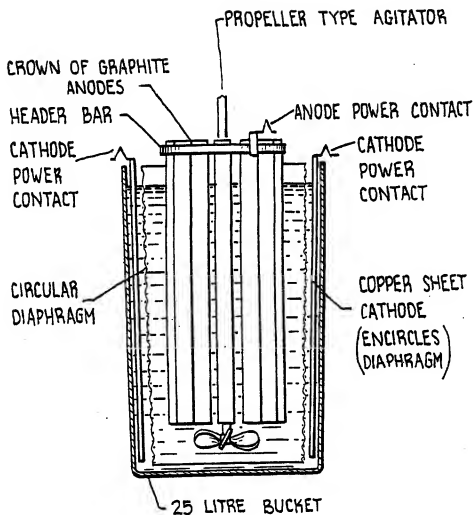


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16. A process according to Claim 15 wherein the oxidation potential of the solution is maintained above about 850 m.v.
17. A process according to Claim 15 wherein the catholyte compartment has a volume which is smaller than that of the anolyte compartment.
18. A process according to Claim 15 wherein said mixture is agitated in the anolyte compartment.
19. A process according to Claim 15 wherein the current is intermittently between the anode and cathode.



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INTERNATIONAL SEARCH REPORT

International Application No PCT/AU 83/00098

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ¹ According to International Patent Classification (IPC) or to both National Classification and IPC Int. Cl. ³ C22B 11/06, 11/04, C25C 5/02		
II. FIELDS SEARCHED Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
IPC	C22B 11/06, 11/04, C25C 5/02, 1/20	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁴		
AU: IPC as above plus C22B 3/00; Australian Classification 14.361, 14.35, 14.51, 14.52		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category ¹⁵	Citation of Document, ¹⁴ with Indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
X	AU, B, 54656/73 (466261) (CYPRUS METALLURGICAL PROCESSES CORP.) 24 October 1974 (24.10.74) See Page and Examples 6 & 7.	1,2,4,9,15, 16
X	US, A, 3772003 (GORDY) 13 November 1973 (13.11.73) See Example 1.	1,2,6,15,16, 17
X	US, A, 3639925 (SCHEINER ET AL) 8 February 1972 (08.02.72)	1,2,4,5,6
Y	GB, A, 1277263 (EASTMAN KODAK COY) 7 June 1972 (07.06.72)	1,2,15
X,Y	US, A, 3957603 (RHODES) 18 May 1976 (18.05.76)	1 & 15
Y	AU, A, 52038/73 (AUSTRALIAN MINERAL DEVELOPMENT LABORATORIES) 15 August 1974 (15.08.74)	1,2,15,16, 17,18
Y	WO, A, 82/01195 (DEXTEC METALLURGICAL PTY. LTD.) 15 April 1982 (15.04.82) (& AU, A, 75848/81, & EP, A, 61468)	1-5
Y	US, A, 2835569 (F. REYNAUD et al) 20 May 1958 (20.05.58) (& GB, A, 795790)	1-5
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IV. CERTIFICATION Date of the Actual Completion of the International Search ¹ 17 October 1983 (17.10.83) International Searching Authority ¹ Australian Patent Office		
Date of Mailing of this International Search Report ¹ 26 October 1983 (26-10-83) Signature of Authorized Officer ¹⁸ A.S. Moore <i>A.A. Moore</i>		